APPLICATION FOR
UNITED STATES PATENT

in the name of

Paul A. Christian, Zhiping Jiang, William L. Bowden, and Klaus Brandt

For

PRIMARY LITHIUM ELECTROCHEMICAL CELL

Fish & Richardson P.C.
601 Thirteenth Street, NW
Washington, DC 20005
Tel.: (202) 783-5070
Fax: (202) 783-2331

ATTORNEY DOCKET:

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PRIMARY LITHIUM ELECTROCHEMICAL CELL

TECHNICAL FIELD

This invention relates to a primary lithium electrochemical cell and a method of manufacturing a primary lithium electrochemical cell.

BACKGROUND

5   A battery includes one or more galvanic cells (i.e., cells that produce a direct current of electricity) in a finished package. Cells of this type generally contain two electrodes separated by a medium capable of transporting ions, called an electrolyte. Typical electrolytes include liquid organic electrolytes or a polymeric electrolytes. The cell produces electricity from chemical reactions through oxidation at one electrode, commonly referred to

10   as the negative electrode or anode, and reduction at the other electrode, commonly referred to as the positive electrode or cathode. Completion of an electrically conducting circuit including the negative and positive electrodes allows ion transport across the cell and discharges the battery. A primary battery is intended to be discharged to exhaustion once, and then discarded. A rechargable battery can be discharged and recharged multiple times.

15   An example of a primary battery is a primary lithium cell. A lithium electrochemical cell is a galvanic cell using lithium, a lithium alloy or other lithium containing materials as one electrode in the cell. The other electrode of the cell can include, for example, a transition metal oxide, such as gamma-manganese dioxide (γ-manganese dioxide or γ-MnO$_2$) or transition metal sulfide such as iron disulfide. The metal oxide or sulfide used in the

20   electrode can be processed prior to use in a lithium battery. Generally, γ-manganese dioxide can be prepared by chemical methods or electrochemical methods. The resulting materials are known as chemically produced γ-manganese dioxide (CMD) and electrochemically produced (e.g., electrolytic or electrodeposited) γ-manganese dioxide (EMD), respectively.

SUMMARY

25   A primary electrochemical cell includes a cathode including lambda-manganese dioxide (λ-MnO$_2$) having a spinel-related crystal structure. The anode can include lithium metal or a lithium alloy, such as lithium aluminum alloy.

In one aspect, a primary lithium electrochemical cell includes a cathode including lambda-manganese dioxide, an anode including lithium, a separator between the anode and the cathode, and an electrolyte contacting the cathode, the anode and the separator. The cell has an average closed circuit voltage (CCV) between 3.8 and 4.1V and a specific discharge capacity to a 3V cutoff of greater than about 130 mAh/g at a nominal discharge rate of 1 mA/cm^2. The cell can have a 3V cutoff of greater than 135 mAh/g or 140 mAh/g or greater at a nominal discharge rate of 0.4 mA/cm^2.

The lambda-manganese dioxide can be heated to a temperature of less than 150°C, or 120°C or less, during processing and cathode fabrication.

In another aspect, a method of preparing lambda-manganese dioxide includes contacting water with a compound having the general formula $Li_{1+x}Mn_{2-x}O_4$, wherein x is from –0.02 to +0.02, or -0.005 to +0.005, adding an acid to the mixture of water and the compound until the water has a pH of 1 or less, preferably between 0.5 and 1, separating a solid product from the water and acid, and drying the solid at a temperature of 150°C or less to obtain the lambda-manganese dioxide. The method can include washing the solid separated from the water and acid with water until the washings have a pH of between 6 and 7.

The compound can have a BET surface area of between 1 and 10 m^2/g, or greater than 4 m^2/g or greater than 8 m^2/g, a total pore volume of between 0.02 and 0.2, or 0.05 and 0.15, cubic centimeters per gram, or an average pore size of between 100 and 300 Å.

The solid can be dried at a temperature between 20°C and 120°C, 30°C and 90°C, or between 50°C and 70°C. A vacuum optionally can be applied during drying.

Contacting water and the compound includes forming a slurry. The slurry can be maintained at a temperature below 50°C or between about 10°C and 50°C, or about 15°C to 30°C. The acid can be sulfuric acid, nitric acid, perchloric acid, hydrochloric acid, toluenesulfonic acid or trifluoromethylsulfonic acid. The acid solution can have a concentration between 1 and 8 molar. The temperature of the slurry can be held substantially constant during the addition of the acid.

In another aspect, a method of manufacturing a primary electrochemical cell includes providing a positive electrode including lambda-manganese oxide and forming a cell including the positive electrode and a negative electrode including lithium. The cell has a

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closed circuit voltage between 3.8V and 4.1V and a specific discharge capacity to a 3V cutoff of greater than about 130 mAh/g at a nominal discharge rate of 1 mA/cm^2. Providing the electrode can include preparing lambda-manganese dioxide by a method including contacting water with a compound of the formula $Li_{1+x}Mn_{2-x}O_4$, wherein x is from –0.02 to

5   +0.02, adding an acid to the water and compound until the water has a pH of 1 or less, separating a solid from the water and acid, and drying the solid at a temperature of 150°C or below to obtain the lambda-manganese dioxide. The electrode can be fabricated by mixing the lambda-manganese dioxide with a conductive additive and an optional binder.

A primary lithium electrochemical cell including a cathode containing λ-MnO_2 can

10   have an average closed circuit voltage of between 3.8V and 4.1V, a specific discharge capacity to a 3V cutoff of greater than 135 mAh/g at a discharge rate of 1 mA/cm^2, good high-rate performance, and adequate capacity retention when stored. A closed circuit voltage of about 4V can provide desirable voltage compatibility with lithium-ion secondary cells having cathodes containing $LiCoO_2$, $LiNiO_2$ or solid solutions thereof (i.e. $LiCo_xNi_{1-x}O_2$,

15   wherein 0<x<1). A specific single cycle capacity of greater than 135 mAh/g can provide greater capacity than the average single cycle capacity for a typical lithium-ion secondary cell having a cathode containing $LiCoO_2$, $LiNiO_2$ or solid solutions thereof. Adequate capacity retention when stored can be especially important because in a primary electrochemical cell any loss of capacity cannot be recovered through recharging. A primary

20   lithium electrochemical cell having a cathode including λ-MnO_2 can have a higher total energy density than a primary lithium electrochemical cell having a cathode including heat-treated γ/β-MnO_2 and having an average closed circuit voltage of about 2.8V.

The physical and chemical properties of a lithium manganese oxide spinel powder ($LiMn_2O_4$) used as a precursor for the λ-MnO_2, especially the chemical stoichiometry and the

25   particle microstructure, can dramatically influence the 4V discharge capacity and the thermal stability of the resulting λ-MnO_2 product. A high-capacity λ-MnO_2 can be produced by substantially completely removing of lithium from the spinel lattice of a nominally stoichiometric precursor spinel, for example, by treating the spinel with acid to a pH value of less than 2. By avoiding heat treatment of the λ-MnO_2 powder above 150°C, for example in

30   the range of 80°C to 120°C, decomposition of the λ-MnO_2 can be reduced or avoided,

leading to a specific capacity for a low-rate discharge of greater than 130 mAh/g to a 3V

cutoff, but less than the theoretical 4V capacity of about 154 mAh/g.

Other features and advantages of the invention will be apparent from the description

of the preferred embodiments and from the claims.

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DESCRIPTION OF DRAWINGS

Figure 1 is a cross-section view of a wound lithium primary electrochemical cell.

Figure 2 is a graph depicting a comparison of x-ray powder diffraction patterns for λ-

MnO_2 powders and the nominally stoichiometric spinel precursor powder.

Figure 3 is a graph depicting the discharge performance of primary lithium

10   electrochemical cells discharged at 1 mA/cm^2 (i.e., C/45) to a 3V cutoff.

Figure 4 is a graph depicting a comparison of the discharge performance of primary

lithium electrochemical cells discharged at either 0.4 mA/cm^2 or 1 mA/cm^2 to a 3V cutoff.

Figure 5 is a graph depicting the incremental discharge capacity distribution for a

primary lithium electrochemical cell having a cathode including λ-MnO_2 by Stepped

15   Potential Electro-Chemical Spectroscopy (SPECS).

Figure 6 is a graph depicting the discharge performance of primary lithium

electrochemical cells having cathodes containing λ-MnO_2 heat-treated in vacuum at either

120°C or 150°C *in vacuo* for 4 hrs.

DETAILED DESCRIPTION

20   Referring to Figure 1, a lithium primary electrochemical cell 10 that includes anode

12 in electrical contact with a negative lead 14, a cathode 16 in electrical contact with a

positive lead 18, a separator 20 and an electrolyte solution. Anode 12, cathode 16, separator

20 and the electrolyte solution are contained within housing 22. The electrolyte solution

includes a solvent system and a salt that is at least partially dissolved in the solvent system.

25   One end of housing 22 is closed with a cap 24 and an annular insulating gasket 26 that can

provide a gas-tight and fluid-tight seal. Positive lead 18 connects anode 16 to cap 24. A

safety valve 28 is disposed in the inner side of cap 24 and is configured to decrease the

pressure within battery 10 when the pressure exceeds some predetermined value.

Electrochemical cell 10 can be, for example, a cylicdrical wound cell, a button or coin cell, a

30   prismatic cell, a rigid laminar cell or a flexible pouch, envelope or bag cell.

Anode 12 can include alkali and alkaline earth metals, such as lithium, sodium, potassium, calcium, magnesium, or alloys thereof. The anode can include alloys of alkali or alkaline earth metals with another metal or other metals, for example, aluminum. An anode including lithium can include elemental lithium or lithium alloys, or combinations thereof.

The electrolyte solution includes a solvent and a salt. The salt can be an alkali or alkaline earth salt such as a lithium salt, a sodium salt, a potassium salt, a calcium salt, a magnesium salt, or combinations thererof. Examples of lithium salts include $LiPF_6$, $LiBF_4$, $LiAsF_6$, $LiClO_4$, LiI, $LiBr$, $LiAlCl_4$, $LiCF_3SO_3$ $LiN(CF_3SO_2)_2$, $Li(C_4F_9SO_2NCN)$, and $LiB(C_6H_4O_2)_2$. The solvent can be an organic solvent. Examples of organic solvents include cyclic carbonates, chain carbonates, ethers, esters, alkoxy alkanes, nitriles and phosphates. Examples of cyclic carbonates include ethylene carbonate and propylene carbonate. Examples of chain carbonates include dimethyl carbonate, diethyl carbonate and ethylmethyl carbonate. Examples of ethers include diethyl ether and dimethyl ether. Examples of esters include methyl propionate, ethyl propionate, methyl butyrate and gamma butyrolactone. Examples of alkoxy alkanes include dimethoxy ethane and diethoxy ethane. Examples of nitriles include acetonitrile. Examples of phosphates include triethyl phosphate and trimethyl phosphate. The electrolyte can be a polymeric electrolyte.

The concentration of the salt in the electrolyte solution can range from about 0.01 molar to about 3 molar, more preferably from about 0.5 molar to about 1.5 molar, and most preferably about 1 molar.

Separator 20 can be formed of any of the standard separator materials used in lithium primary or secondary batteries. For example, separator 20 can be formed of polypropylene, polyethylene, a polyamide (e.g., a nylon), a polysulfone and/or a polyvinyl chloride. Separator 20 can have a thickness of from about 0.1 millimeters to about 2 millimeters, and more preferably from about 0.2 millimeters to about 0.5 millimeters.

Separator 20 can be cut into pieces of a similar size as anode 12 and cathode 16 and placed therebetween as shown in Figure 1. Anode 12, cathode 16 and separator 20 can then be placed within housing 22 which can be made of a metal such as nickel or nickel plated steel, stainless steel, aluminum-clad stainless steel, or a plastic such as polyvinyl chloride, polypropylene, a polysulfone, ABS or a polyamide. Housing 22 containing anode 12, cathode 16 and separator 20 can be filled with the electrolytic solution and subsequently hermetically sealed with cap 24 and annular insulating gasket 26.

Cathode 16 includes an active cathode material that can undergo alkali ion insertion during discharge of battery 10. The cathode can also include a binder, for example, a polymeric binder such as PTFE, PVDF or Viton. The cathode can also include a carbon source, such as, for example, carbon black, synthetic graphite including expanded graphite or non-synthetic graphite including natural graphite, an acetylenic mesophase carbon, coke, graphitized carbon nanofibers or a polyacetylenic semiconductor.

The active cathode material includes lambda-manganese dioxide (λ-MnO_2), which can be synthesized by an oxidative delithiation process from a stoichiometric lithium manganese oxide spinel ($LiMn_2O_4$) precursor prepared by various synthetic methods and having differing physical properties. A suitable lithium manganese oxide spinel can be prepared as described in, for example, U.S. Patent Nos. 4,246,253; 4,507,371; 4,828,834; 5,245,932; 5,425,932, 5,997,839, or 6,207,129, each of which is incorporated by reference in its entirety. More particularly, the lithium manganese oxide spinel can have a formula of $Li_{1+x}Mn_{2-x}O_4$, where $-0.02 < x < +0.02$. Alternatively, a suitable stoichiometric lithium manganese oxide spinel can be obtained, for example, from Kerr-McGee Chemical LLC, Oklahoma City, Oklahoma, Carus Chemical Co., Peru, Illinois, or Erachem-Comilog, Inc., Baltimore, Maryland.

Physical, microstructural, and chemical properties for commercial samples of $LiMn_2O_4$-type spinels obtained from three different suppliers are summarized in Table 1. The x-ray powder diffraction (XRD) patterns for the $LiMn_2O_4$-type spinel powders were measured using a Rigaku Miniflex diffractometer using Cu K_α radiation. The spinel powder from Carus Chemical has the largest refined cubic lattice cell constant, a_0, and also has a chemical composition very close to that for stoichiometric $LiMn_2O_4$ spinel. The reported (e.g., ICDD PDF No. 35-0782) cubic lattice constant for stoichiometric $LiMn_2O_4$ spinel is 8.248 Å. The other spinel powders from Kerr-McGee and Erachem (viz., Chemetals) have XRD powder patterns that give refined lattice constants of 8.231Å and 8.236 Å, respectively. These latter a_0 values are more consistent with those values typically reported for spinels having a slight excess lithium stoichiometry (i.e., $Li_{1+x}Mn_{2-x}O_4$, where $0 < x < 0.1$). The a_0 values for such spinels decrease linearly as x increases for x values between -0.15 and 0.25. See, for example, U.S. Patent No. 5,425,932, which is incorporated by reference in its entirety.

The oxidative delithiation process can include, for example, the following steps:
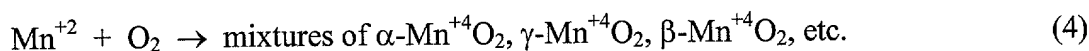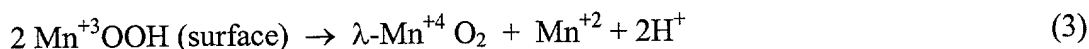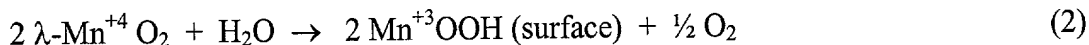
1. A slurry of the precursor spinel powder is formed with stirring in distilled or deionized water and adjusted to a temperature between about 10 and 50°C, preferably between about 15°C and 30°C;

2. An aqueous solution of an acid, such as, for example, sulfuric acid, nitric acid, hydrochloric acid, perchloric acid, toluenesulfonic acid or trifluoromethylsulfonic acid, is added to the slurry with constant stirring at a rate to maintain a constant slurry temperature until the pH of the slurry stabilizes at a value typically below about 2, below about 1, or below about 0.7 but greater than about 0.5, and remains constant at this value for at least 0.75 hour (optionally, stirring can be continued for up to an additional 24 hours);

3. The solid product is separated from the supernatant liquid, for example, by suction, pressure filtration, or centrifugation, and is washed with aliquots of distilled or deionized water until the washings have a neutral pH (e.g., between about 6-7); and

4. The solid product is dried *in vacuo* for between 4 and 24 hours at 30 to 120°C, preferably at 50 to 90°C, or more preferably at 60°C to 70°C.

After processing, the dried solid typically exhibits a weight loss of about 27 wt% relative to the initial weight of the precursor $LiMn_2O_4$ spinel powder. The total lithium content of the stoichiometric $LiMn_2O_4$ spinel is about 3.8 wt%. The expected total weight loss is about 28 wt%. The observed weight loss can be attributed to dissolution of lithium ions that migrated to the surface of the spinel particles as well as Mn^{+2} ions from the $LiMn_2O_4$ spinel crystal lattice putatively resulting from a disproportionation reaction whereby Mn^{+3} ions on the surface of the spinel particles are converted to insoluble Mn^{+4} ions that remain on the surface and soluble Mn^{+2} ions that dissolve in the acid solution according to Equation 1:

$$2LiMn^{+3}Mn^{+4}O_4 + 4H^+ \rightarrow 3\ \lambda\text{-}Mn^{+4}O_2 + Mn^{+2} + 2Li^+ + 2H_2O \qquad (1)$$
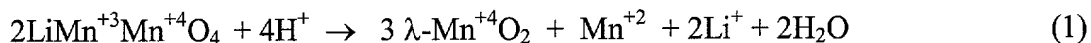
Maintaining the temperature of the acid solution below about 55°C during the delithiation process can minimize the formation of undesirable manganese oxide side-products that can form by re-oxidation by oxygen of the aqueous Mn^{+2} ions. For example, the dissolution of $\lambda\text{-}MnO_2$ can proceed by a mechanism whereby $\lambda\text{-}MnO_2$ is reduced by water according to Equation 2. The resulting Mn^{+3} ions formed on the surface of the $\lambda\text{-}MnO_2$ particles can disproportionate according to Equation 3 to form soluble Mn^{+2} ions and
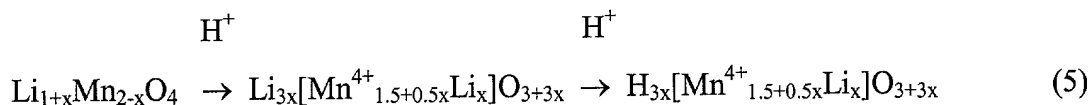
insoluble Mn^{+4}. The soluble Mn^{+2} ions can be reoxidized according to Equation 4 by air as well as by oxygen generated during the reduction of λ-MnO_2 to form undesirable manganese oxide products that can deposit on the surface of the remaining λ-MnO_2 particles (see, Equation 2-4).

$$2\ \lambda\text{-}Mn^{+4}O_2\ +\ H_2O\ \rightarrow\ 2\ Mn^{+3}OOH\ (surface)\ +\ \tfrac{1}{2}\ O_2 \tag{2}$$

$$2\ Mn^{+3}OOH\ (surface)\ \rightarrow\ \lambda\text{-}Mn^{+4}O_2\ +\ Mn^{+2}\ +\ 2H^+ \tag{3}$$

$$Mn^{+2}\ +\ O_2\ \rightarrow\ \text{mixtures of } \alpha\text{-}Mn^{+4}O_2,\ \gamma\text{-}Mn^{+4}O_2,\ \beta\text{-}Mn^{+4}O_2,\ etc. \tag{4}$$

The x-ray diffraction patterns for the λ-MnO_2 powders were measured using a Rigaku Miniflex diffractometer using Cu K_α radiation. The XRD powder patterns for the various dried λ-MnO_2 powders are consistent with that reported for λ-MnO_2 (e.g., ICDD PDF No. 44-0992). *See*, U.S. Patent No. 4,246,253, which is incorporated by reference in its entirety. The lattice constants, a_0, for the refined cubic unit cells for the samples of λ-MnO_2 prepared by the method described above are given in Table 1. The a_0 values range between 8.035 and 8.048 Å. T. Ohzuku *et al.* have reported (See J. Electrochem. Soc., Vol. 137, 1990, pp. 769) that the refined cubic lattice constant a_0, can be correlated with the residual lithium content in the λ-MnO_2 lattice (i.e., the smaller the a_0 value, the less lithium present). Figure 2 is a graph depicting a comparison of x-ray powder diffraction patterns for λ-MnO_2 powders prepared by either 0.75 or 16 hours of acid treatment of a precursor spinel and the corresponding precursor spinel powder from Kerr-McGee having a nominal excess lithium stoichiometry of $Li_{1.05}Mn_{1.95}O_4$. The XRD powder pattern for λ-MnO_2 is distinguishable from that for the corresponding precursor spinel as shown in Figure 2 for a sample of precursor spinel having a nominal excess lithium stoichiometry of $Li_{1.05}Mn_{1.95}O_4$ and the corresponding λ-MnO_2 acid-treated for either 0.75 or 16 hours at 15°C by a shift in the diffraction peak positions to higher 2-theta angles for λ-MnO_2.

The precursor spinel can have a nominally stoichiometric composition, for example, a composition having the formula $Li_{1+x}Mn_{2-x}O_4$, wherein x is from −0.02 to +0.02, such as $Li_{1.01}Mn_{1.99}O_4$, from which more complete delithiation can be accomplished, and in general, replacement of the lithium ions with protons by an ion-exchange process, such as that shown in equation 5, can be reduced or avoided. The presence of protons in lattice sites formerly occupied by lithium ions is theorized by the present inventors to result in thermal instability

and decreased discharge capacities for lithium cells having cathodes including such materials.

$$H^+ \qquad\qquad H^+$$

$$Li_{1+x}Mn_{2-x}O_4 \rightarrow Li_{3x}[Mn^{4+}_{1.5+0.5x}Li_x]O_{3+3x} \rightarrow H_{3x}[Mn^{4+}_{1.5+0.5x}Li_x]O_{3+3x} \qquad (5)$$

where $0.02 < x < 0.33$

Specific surface areas of the various λ-MnO_2 powders as determined by multipoint nitrogen adsorption isotherms by the B.E.T. method as described by P. W. Atkins in "Physical Chemistry", 5th ed., New York: W. H. Freeman & Co., 1994, pp. 990-2. BET measurements were found to be substantially greater than those for the corresponding precursor spinel powders. *See*, Table 1. This increase in specific surface area is consistent with apparent increased roughness or porosity in the surface microstructure of the particles observed by comparing SEM micrographs (10,000X) of particles of the precursor spinel, for example, and particles of the corresponding λ-MnO_2. Further, porosimetric measurements on a precursor spinel powder and the corresponding λ-MnO_2 powder revealed that the total pore volume more than doubled after de-lithiation to λ-MnO_2 and that the average pore size decreased by nearly 80%.

Table 1

Precursor Spinel	Spinel A	Spinel B	Spinel C
Lattice constant, a_o Spinel (Å)	8.231	8.242	8.236
Lattice constant, a_o λ-MnO_2 (Å)	8.048	8.035	8.041
BET SSA, Spinel (m^2/g)	0.44	3.43	1.78
BET SSA, λ-MnO_2 (m^2/g)	4.98	8.30	7.21
Ave particle size, Spinel (μm)	12	14.6	28.5
Average Pore Size, Spinel (Å)		157	
Average Pore Size, λ-MnO_2 (Å)		36.5	
Total Pore Volume, Spinel (cc/g)		0.05	
λ-MnO_2 Total Pore Volume (cc/g)		0.11	
Tap Density, Spinel (g/cm^3)	2.10	2.08	1.96
Spinel Stoichiometry, $Li_{1+x}Mn_{2-x}O_4$, x = ?	0.06-0.08	0.01	>0.02
True Density, Spinel (g/cm^3)	4.225	4.196	4.219
True Density, λ-MnO_2 (g/cm^3)	4.480	4.442	4.611

In certain embodiments, precursor spinels that permit preparation of λ-MnO_2 in accordance with the present invention can be selected according to the following selection

criteria: (1) general chemical formula is $Li_{1+x}Mn_{2-x}O_4$ wherein x ranges from –0.05 to +0.05, preferably from –0.02 to +0.02, more preferably from –0.005 to +0.005; (2) BET surface area of the precursor spinel powder is between about 1 and 10 m^2/g; (3) total pore volume of the precursor spinel powder is between about 0.02 and 0.1 cubic centimeters per gram; and (4) average pore size of the precursor spinel powder is between about 100 and 300 Å.

The thermal stability of the λ-MnO_2 powder prepared by the method of the invention was evaluated in order to determine the effects of various thermal treatments during cathode fabrication (e.g., drying, coating, pressing, etc.) on cell discharge performance. The XRD powder patterns for a sample of λ-MnO_2 powder heated *in vacuo* at 120°C for 4 hours was found to be identical to that for a bulk sample of λ-MnO_2 powder originally dried *in vacuo* at 70°C for up to 16 hours, indicating suitable thermal stability at this temperature. The XRD powder pattern for a sample of λ-MnO_2 powder heated *in vacuo* at 150°C for 4 hours exhibited a slight broadening of the λ-MnO_2 peaks as well as the appearance of a new broad peak at a 2θ angle of about 20° indicating the onset of decomposition of the λ-MnO_2 phase. Heating a sample of λ-MnO_2 powder *in vacuo* at 180°C for 4 hours resulted in the complete disappearance of the characteristic λ-MnO_2 peaks and the appearance of several broad peaks in the XRD pattern suggesting the formation of one or more new phases. These poorly-resolved new peaks can be attributed to the presence of a mixture of β-MnO_2 and ϵ-MnO_2 phases.

In addition to evaluating the thermal stability of the λ-MnO_2 powder, the thermal stability of λ-MnO_2 in pressed composite cathodes also containing a conductive carbon and a binder was evaluated. XRD patterns for pressed composite cathodes after heating for 4 hours at 120°C showed a broadening of the λ-MnO_2 peaks as well as the appearance of several new, broad, weak peaks attributed to the ϵ-MnO_2 phase indicating the onset of decomposition of the λ-MnO_2 phase. Thus, λ-MnO_2 in the pressed composite cathode appears to start decomposing at an even lower temperature than λ-MnO_2 powder alone. In XRD patterns for cathodes heated at 150°C or 180°C, all of the peaks attributed to the λ-MnO_2 phase disappeared completely, and only broad peaks characteristic of the ϵ-MnO_2 phase were present. Furthermore, unlike the case of λ-MnO_2 powder, no peaks for the β-MnO_2 phase could be discerned in the XRD pattern for a composite cathode heated at 180°C.

Lithium primary cells including composite cathodes containing λ-MnO_2 were prepared according to the following representative examples.

EXAMPLE 1

Approximately 120 g of a nearly stoichiometric spinel B having a nominal composition of $Li_{1.01}Mn_{1.99}O_4$ (Carus Chemical Co.) was added with stirring to about 200 ml distilled water to form an aqueous slurry that was cooled to 15°C. 6M H_2SO_4 was added dropwise with constant stirring until the pH of the slurry stabilized at about 0.7. The slurry was stirred for an additional 20 hours at pH 0.7. The rate of acid addition was adjusted so as to maintain the temperature of the slurry at 15°C. The solid was separated from the liquid by either pressure or suction filtration through a non-woven, spun-bonded polyethylene film (Dupont, Tyvek) and washed with aliquots of distilled water until the washings had a neutral pH (e.g., a pH of about 6). The solid filtercake was dried *in vacuo* for 4-16 hours at 70°C. The weight of the dried λ-MnO_2 product was about 87 g, which corresponds to a weight loss of about 27.5%.

Samples of dried λ-MnO_2 powder were mixed with carbon black (Chevron SAB/C55) as a conductive additive and PTFE powder (Dupont 601A) as a binder in a weight ratio of 60:10:30 in a laboratory blender to form a cathode mix. Portions (~0.5 g) of the cathode mix were pressed into composite cathode disks about 17.5 mm in diameter (i.e., ~2.5 cm^2 in area) and inserted into stainless steel test cells having an effective internal diameter of 17.5 mm thereby simulating a typical lithium coin cell. Such cells also have limited electrolyte volume, electrodes in close geometric proximity, and a positive pressure (e.g., 2 kg/cm^2) applied to the electrodes by a coil spring inside the cell. The design of the test cell is similar to that described by Geronov *et al.*, in J. Electrochem. Soc., Vol. 137, No. 11, 1990, pp. 3338-3344, which is incorporated herein by reference in its entirety. A disk punched from lithium metal foil 1 mm thick served as the anode. The electrolyte solution was 1M $LiPF_6$ in 1:1, v/v EC:DMC (EM Industries, ZV1020) as typically used in secondary lithium-ion cells. A separator sheet in the form of a disk was saturated with electrolyte solution and placed on top of the cathode disk. Additional electrolyte was added to ensure complete wetting of the cathode disk.

The spring-loaded cells of Example 1a with cathodes containing λ-MnO_2 prepared from the spinel B were discharged at a nominal constant current of 1 mA corresponding to a

current density of 0.4 mA/cm^2 and a nominal discharge rate of about C/45. These cells were discharged to cutoff voltages of 3.5V or 3V. Gravimetric or specific (viz., mAh/g) discharge capacities for the cells of Example 1a of about 135 mAh/g to 3V and 133 mAh/g to 3.5V were obtained. See Table 2. Also, the discharge curve for the cells of Example 1a exhibited two distinct, flat plateaus at about 4.05V and about 3.95V, as shown in Figure 3.

Another cathode mix was prepared by mixing λ-MnO$_2$ dried at 70°C for 4 hours with carbon black (viz., Chevron SAB/C55) as a conductive additive and of PTFE powder (e.g., DuPont 601A) as a binder in a weight ratio of 75:10:15 in a laboratory blender. Portions (~0.5 g) of the cathode mix were pressed into cathode disks that were inserted into several spring-loaded cells. The spring-loaded cells of Example 1b with cathodes containing λ-MnO$_2$ prepared from spinel B were discharged at a constant current of 2.5 mA, corresponding to a current density of 1 mA/cm^2 and a nominal discharge rate of C/25. The cells were discharged to cutoff voltages of 3.5V or 3V. Gravimetric discharge capacities of about 137 mAh/g to 3V and 134 mAh/g to 3.5V were obtained for the cells of Example 1b. See Table 2.

COMPARATIVE EXAMPLE 1

Samples of λ-MnO$_2$ were prepared in the same manner as described in Example 1 except that spinel A having the nominal composition Li$_{1.06}$Mn$_{1.94}$O$_4$ (Kerr-McGee, #210) was employed. A cathode mix prepared by mixing λ-MnO$_2$ dried at 70°C for 4 hours with carbon black (viz., Chevron SAB/C55) as a conductive additive and PTFE powder (viz., DuPont 601A) as a binder in a weight ratio of 60:10:30 in a laboratory blender. Portions (~0.5 g) of the mix were pressed into composite cathode disks that were inserted into several spring-loaded cells. The cells were discharged at a constant current of 1 mA to a cutoff voltage of 3V or 3.5V. The average open circuit voltage for freshly assembled cells was about 4.15V. Gravimetric discharge capacities of about 116 mAh/g to 3V and 113 mAh/g to 3.5V were obtained. See Table 2. Similar to the discharge curves for the cells of Example 1, the discharge curves for cells of Comparative Example 1 exhibited two distinct, flat plateaus at about 4.05V and about 3.95V as shown in Figure 4.

COMPARATIVE EXAMPLE 2

Samples of λ-MnO$_2$ were prepared in the same manner as described in Example 1 except that spinel B having a nominally stoichiometric composition (Erachem/Chemetals,

LMO-800E) was employed. A cathode mix prepared by mixing λ-MnO₂ dried at 70°C for 4

hours with carbon black (viz., Chevron SAB/C55) as a conductive additive and PTFE

powder (viz., DuPont 601A) as a binder in a weight ratio of 85:5:10 in a laboratory blender.

Portions (~0.5 g) of the mix were pressed into composite cathode disks that were inserted

5   into several spring-loaded cells. The cells were discharged at a constant current of 2.5 mA to

a cutoff voltage of 3V or 3.5V. The average open circuit voltage for freshly assembled cells

was about 4.17V. Gravimetric discharge capacities of about 120 mAh/g to 3V and 105

mAh/g to 3.5V were obtained. *See* Table 2. Unlike the discharge curves for the cells of

Example 1, the discharge curves for the cells of Comparative Example 2 did not have two

10   distinct, flat plateaus at about 4.05V and about 3.95V, but instead exhibited a sloping

discharge profile as shown in Figure 4.

EXAMPLE 2

Samples of λ-MnO₂ composite cathodes were prepared in the same manner as

described in Example 1 except that they were heat-treated *in vacuo* at 120°C for 4 hours (Ex.

15   2a) or 16 hours (Ex. 2b) or at 150°C for 4 hours (Ex. 2c) before being inserted in lithium

spring-loaded cells. These cells were discharged continuously at a constant current of 1 or

2.5 mA to a cutoff voltage of 3.5V and the resulting gravimetric discharge capacities given in

Table 2. A comparison of the 4V plateau discharge capacities with those obtained for cells

having λ-MnO₂ cathodes dried at 70°C with no further heat-treatment clearly indicates that

20   heat-treatment at 120°C for 16 hours substantially degrades the 4V capacity. Heat-treatment

at 150°C for only 4 hours results in complete loss of 4V capacity. This loss of 4V capacity is

dramatically depicted in Figure 6.

Typical discharge curves for cells containing the λ-MnO₂ samples prepared from

various commercial spinels are shown in Figure 4. Lithium cells with composite cathodes

25   containing λ-MnO₂ from spinel C discharged to a 3V cutoff at a nominal rate of about 1.0

mA/cm² gave specific capacities of about 120 mAh/g. Under similar discharge conditions,

cells with composite cathodes containing λ-MnO₂ prepared from the spinel B gave a

substantially greater specific capacity of about 135 mAh/g. Cells with composite cathodes

containing λ-MnO₂ prepared from spinel A gave even lower specific capacities of about 115

30   mAh/g even at a substantially lower nominal discharge rate of about 0.4 mA/cm². Further,

the discharge curves for cells containing λ-MnO₂ prepared from spinel A and spinel B both

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exhibit two distinct, relatively flat plateaus at about 4.05V and 3.95V similar to those typically observed for an electrochemically-charged spinel. In contrast, discharge curves for cells containing λ-MnO$_2$ prepared from spinel C exhibit a single sloping plateau in the 4V region with an average CCV of about 3.9V. Based on the discharge data for cells shown in Figure 4, the λ-MnO$_2$ prepared from spinel B clearly provides superior low-rate discharge performance compared to λ-MnO$_2$ derived from either spinel A or spinel C.

Table 2

Ex. No.	Spinel	Heat Treatment (°C/hours)	Discharge Rate (mA)	Ave OCV (V)	Capacity to 3.5V (mAh/g)	Capacity to 3V (mAh/g)
1a	B	70/4	1	4.18	133	135
1b	B	70/4	2.5	4.14	134	137
C1	A	70/4	1	4.15	113	116
C2	C	70/4	2.5	4.17	105	120
2a	B	120/4	1	4.16	125	---
2b	B	120/16	2.5	4.14	106	
2c	B	150/4	1	3.78	0.5	

In addition, the incremental discharge capacity for a spring-loaded lithium cell having a cathode containing λ-MnO$_2$ of Example 1 was determined using the Stepped Potential Electro-Chemical Spectroscopy (SPECS) method described in detail by Bowden *et al.* in ITE Letters on Batteries, Vol.1, No. 6, 2000, pp. 53-64, which is incorporated herein by reference in its entirety, and depicted in Figure 5. The sharp peaks denoting the incremental capacity resulting from the initial discharge at a nominal sweep rate of 5 mV/hr of the λ-MnO$_2$ cathode material to a cutoff of 3.3V are centered at about 4.05V (peak A) and 3.9V (peak A') indicating the suitability of this material for use in a nominally 4V lithium cell. The relatively low incremental capacity of the broad peak at about 4.15V (peak B) obtained during recharge of the cell to a cutoff of 4.2V and the lack of any incremental capacity for the 4.05V and 3.9V peaks and the broad, low capacity peak centered at about 3.7V (peak C) during the second discharge of the cell to a 3.3V cutoff demonstrate the poor rechargeability of the λ-MnO$_2$ composite cathode. However, the λ-MnO$_2$ composite cathode is particularly suitable for use in primary lithium cells having a lithium metal anode. The inability to

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recharge a cell having a composite cathode containing λ-MnO_2 minimizes potential safety hazards related to re-depositing lithium metal at the anode during recharge and provides a substantial advantage for the 4V lithium primary cells compared to secondary lithium cells having lithium metal anodes.

5   Discharge curves for spring-loaded cells containing λ-MnO_2 cathodes heat-treated at 120°C and 150°C are depicted in Figure 6. The cells were discharged at a nominal rate of 0.4 mA/cm^2 to a 2.0V cutoff. The cells containing the λ-MnO_2 cathodes that were heat-treated at 120°C gave a capacity of 125 mAh/g to a 3.5V cutoff, which is somewhat less than those cells containing non-heat-treated cathodes (e.g., 133 mAh/g). *See* Table 2. The lower

10   capacity presumably is a consequence of some decomposition of the λ-MnO_2 phase during heat-treatment at 120°C as evidenced in the XRD patterns. These cells gave a total capacity of about 235 mAh/g to 2V. The cells containing λ-MnO_2 cathodes heat-treated at 150°C, which actually contained predominantly ε-MnO_2 phase based on the XRD pattern, had an OCV of ~3.7-3.8 V, a CCV of ~2.8 V, and also gave a total capacity of about 240 mAh/g to a

15   2V cutoff. Thus, it appears that all the capacity originally present on the 4 V plateau was shifted down to the 3 V plateau as a result of the heat treatment at 150°C. Therefore, it is necessary to keep processing temperatures below about 100°C during drying, heat-treatment, and cathode fabrication and cell assembly processes in order to maintain the capacity on the 4V plateau.

20   A number of embodiments of the invention have been described. Nevertheless, it will be understood that various modifications may be made without departing from the spirit and scope of the invention. For example, oxidative delithiation of the precursor spinel can be performed using a variety of aqueous oxidizing agents including, for example, an aqueous solution of sodium or potassium peroxydisulfate, sodium or potassium peroxydiphosphate,

25   sodium perborate, sodium or potassium chlorate, sodium or potassium permanganate, cerium (+4) ammonium sulfate or nitrate, or sodium perxenate, or ozone gas bubbled through acidic water. Non-aqueous oxidizing agents include, for example, nitrosonium or nitronium tetrafluoroborate in acetonitrile, nitrosonium or nitronium hexafluorophosphate in acetonitrile, or oleum (i.e., SO_3/H_2SO_4) in sulfolane. Using an aqueous chemical oxidant

30   such as peroxydisulfate, ozone or a non-aqueous oxidizing agent to oxidize the Mn^{+3} ions to Mn^{+4} ions in the $LiMn_2O_4$ spinel can result in substantially less manganese being lost by

dissolution than in the disproportionation process (Equation 1) taking place during treatment with an aqueous acid solution.

Other embodiments are within the scope of the following claims.